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On the role of interfacial segregation on graphite shape in cast irons

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Abstract. Understanding spheroidal graphite growth in cast irons is a long standing problem for which several mechanisms have been proposed. During the last decade, observations using transmission electron microscopy added new information about the stacking of graphite layers, leading eventually to propose other mechanisms than previously thought of such as repeated 2D-nucleation of new growth blocks and their lateral extension at the surface of the spheroids. Furthermore, it has been recently realized that elements known to strongly affect graphite shape are also those that are surface active. This is illustrated here in the case of antimony which is known to lead to spheroidal graphite degeneration when added at some tens of ppm. Using atomic resolution microscopy, segregation of antimony could be evidenced at the graphite/matrix interface of both spheroids and protuberances. This strongly suggests that accumulation of antimony repelled magnesium from the graphite surface until growth of spiky protuberances replaced spheroidal growth.

1. Introduction

Graphitic cast irons are casting alloys with a composite microstructure consisting of graphite precipitates in an iron-based matrix. They are near-eutectic Fe-C-Si alloys containing traces of oxygen and sulphur, and also some manganese due to the recycling of steel scrap. Without treatment of the liquid metal, the graphite appears as large plates when primary and as interconnected lamellae that have grown radially from a nucleus of MnS when eutectic (figure 1a). After addition of 300-500 ppm of magnesium (or rare earths that are however less effective), graphite precipitates as individualised spheroids (figure 1b) around nuclei (oxy-sulphides or nitrides) resulting from appropriate inoculation. It is now widely accepted that graphite spheroids nucleate and start growing in the liquid and get encapsulated within an austenite shell at a later stage of solidification. The change in shape from lamellar to spheroidal graphite gives the cast irons mechanical properties that make them suitable for structural and safety applications, which explains why so much work has been done to understand this.

Graphite spheroids can be classified in the family of spherulites which are found in many materials as well as in the plant world. Granasy *et al.* [1] carried out a study of spherulitic growth and the possibility of modelling it by phase field. However, their approach focused on spherulites whose formation is due to the development of a radial and polycrystalline structure, characterised by repetitive branching. This form of growth was described by Ryschenkow and Faivre [2] in the case of selenium, which is tetragonal and has a c-axis of order 3 like graphite. At very low undercooling, selenium forms monocrystalline platelets elongated in the plane perpendicular to the c axis quite similar to plate-like graphite. These platelets become unstable at increasing undercooling and eventually develop as spherulites following a so-called regular-branching mechanism. In agreement with a scheme proposed by Double and Hellawell [3], Faivre [4] has considered the possibility of formation of a graphite spheroid by a similar succession of crystallographic branching of a graphite flake.



The model just mentioned is one of the very many schemes proposed in the literature for the formation of graphite spheroids in cast irons. Rather than attempting to provide a history of these models, we present in section 2 observations by scanning (SEM) and transmission (TEM) electron microscopy that have clarified some of the ambiguities that the only use of optical microscopy has generated. Excluding schemes incompatible with the described observations, a model based on a 2D nucleation and lateral growth mechanism has been elaborated which will be briefly mentioned. This model pre-supposes the role of magnesium which will be discussed in section 3.

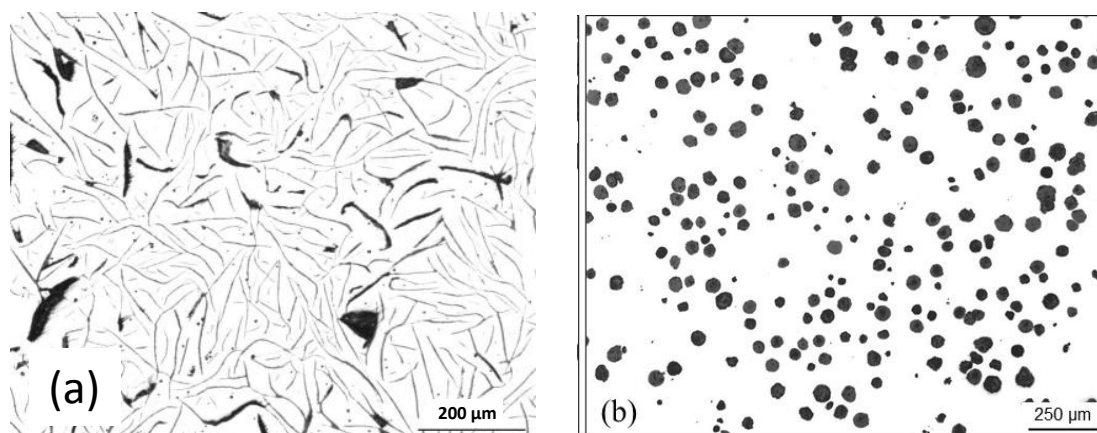


Figure 1. Microstructure of a lamellar graphite (a) and spheroidal graphite (b) iron (courtesy J. Sertucha).

2. The usual structure of graphite spheroids in cast irons

The structure of graphite in cast irons is characterised by the stacking of sheets elongated in the prismatic direction, suggesting that carbon atoms aggregate on these prismatic faces. In the case of flake graphite, these sheets can be several hundred microns long for primary precipitates (figure 2a). Their thickness varies from 50 to 500 nm, and two successive sheets can be rotated around their common c-axis and show low energy configurations for several rotation angles [5]. The observation of this rotation between two successive sheets is a strong indication that a new layer is formed by 2D nucleation on the outer basal surface of the lamella and then grows laterally along the existing surface. This is the mechanism considered by Amini and Abbaschian to model the thickening of primary graphite lamellae [6].

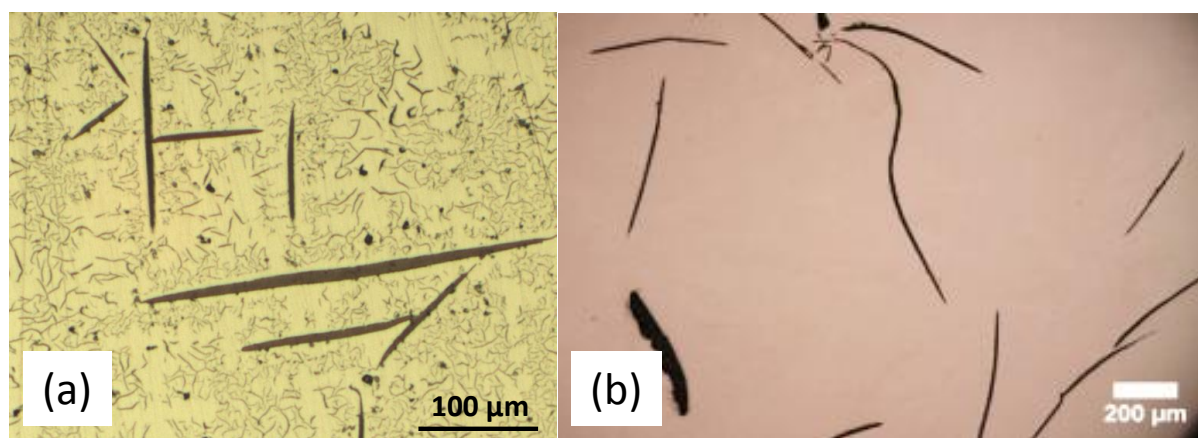


Figure 2. Primary graphite lamellae in a "pure" Fe-C alloy (a) and in a Sb-doped alloy (b). (courtesy of K. Theuwissen)

These possibilities of in-plane rotation should facilitate branching during eutectic growth, but they do not seem to have been reported to influence the shape of the primary precipitates which remain plate-like in "pure" alloys. On the other hand, the addition of certain impurities such as antimony gives a curved appearance to the primary graphite lamellae (see figure 2b) when observed by optical microscopy [7]. TEM observations have shown that such curved lamellae are in fact made up of successive rectilinear blocks that are twisted between each other around an axis parallel to the basal plane. It was then suggested that the antimony accumulates in front of the prismatic planes until it blocks the growth in the initial direction and forces the lamella to take another direction.

Under optical microscopy, and particularly under polarised light, graphite spheroids appear to be formed of adjacent sectors in which the graphite c-axis has a predominantly radial direction (figure 3a). Hillert and Lindholm proposed early on that this arrangement should be associated with growth along screw dislocations [8], a model that has been adopted in many works and is still one of the most frequently presented, together with the slightly modified form of helical growth [3, 9].

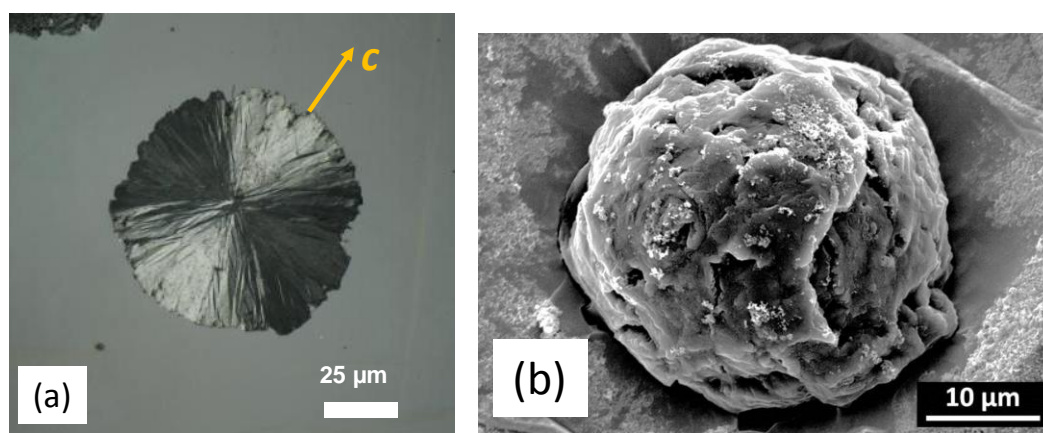


Figure 3. Metallographic section under polarized light (a) and SEM micrograph (b) of a graphite spheroid. The SEM micrograph was taken after deep etching of the matrix. (courtesy of J. Bourdieu)

TEM demonstrated that the graphite in spheroids is also made up of blocks elongated in the prismatic direction, but no longer than a couple of microns [10-12]. The very existence of these blocks stacked one on top of the other is contrary to growth around a screw dislocation, unless we assume that the thickness of the blocks corresponds to the height of the growth step. To get to the bottom of this, the relative orientation of successive blocks was followed in TEM along the radius of a spheroid. The blocks showed a slight disorientation around their common c-axis, but without the expected continuity that should appear in the case of screw dislocation [13] or helical growth. In a very detailed work on structural defects in spheroidal graphite, Qing *et al.* [12] came to the same conclusion of no screw dislocation.

Graphite can take an almost infinite number of forms, which Stefanescu has listed [14]. Although some of these forms may be occasionally encountered in cast irons, most of them are not. This is particularly true of dendritic forms emanating from the nucleus of the spheroids and which, through multiple and successive branching, would explain the formation of the spheroids. If such forms existed, they should be easily observed in the 5-7 µm diameter spheroids found in inoculated castings solidified in 2 or 3 seconds, either by quenching small samples or in the products of centrifugal casting. The absence of these structures or any reminiscences excludes this type of growth. The same is true of lamellar branch structures, which have also been invoked as noticed above. It is worth stressing that the radial lines seen in figure 3a are boundaries between sectors or sub-sectors which have been put in relief during polishing [15].

An alternative scheme for spheroidal graphite growth that ensures a compact stacking of the growth blocks while allowing separate growth of the sectors as in exploded graphite (see next section) was recently proposed [16]. It considers repeated epitaxial nucleation of growth blocks at the surface of the sectors while their lateral extension (along this surface, i.e. in the prismatic direction) is limited by

adsorption of magnesium atoms. Such a model implies that growth of primary graphite proceeds at some undercooling with respect to the graphite liquidus and it has been found to conveniently explain thermal analysis results [17].

What has not yet been sufficiently studied is the formation of the sectors just after the nucleation of the graphite. Theuwissen *et al.* [7] observed the sectors to appear right in contact with the nucleus in large spheroids corresponding to casting at slow cooling rates. There, the graphite layers are slightly disturbed as also observed by Qing *et al.* [18] for smaller spheroids from samples quenched during solidification. These latter authors associate this disorder with the ability of graphite to bend around the nucleus very much as the circumferential model proposed by Sadocha and Gruzleski [19]. This model is contrary to the existence of sectors, and it has been shown that the observation of enveloping leaves on the outer surface of spheroids as illustrated in figure 3b is a surface artefact and does not imply circumferential growth of graphite spheroids [15] as so often claimed. Finally, a couple of works reported the presence of highly disordered graphite in a 500 nm thick zone around the nucleus; this has been discussed previously [20].

3. Role of magnesium

It was mentioned in the introduction that spheroidisation is achieved by adding magnesium or rare earths. Magnesium is much more effective [21] but rare earths (cerium and/or lanthanum) are often added at the same time to enhance the deoxidising and desulphurising effect. However, it has long been established that 200 ppm of magnesium in solution is required for optimum spheroidisation, with the excess going to capture sulphur and oxygen. In itself, this requirement of free magnesium demonstrates that its role is not simply to lower oxygen and sulphur levels, suggesting that it is adsorbed on the surface of graphite and affects its growth forms. Another observation that makes this interaction evident is the fact that over-treatment with magnesium, in practice above 600-800 ppm of added magnesium to the melt, leads to the degeneration of spheroidal graphite (see reviews by Lux [22] and Lacaze *et al.* [23]). This degeneration manifests itself as graphite that appears "exploded" if primary, and as "spiky" or "mesh" graphite if formed during the eutectic transformation; see figure 4.

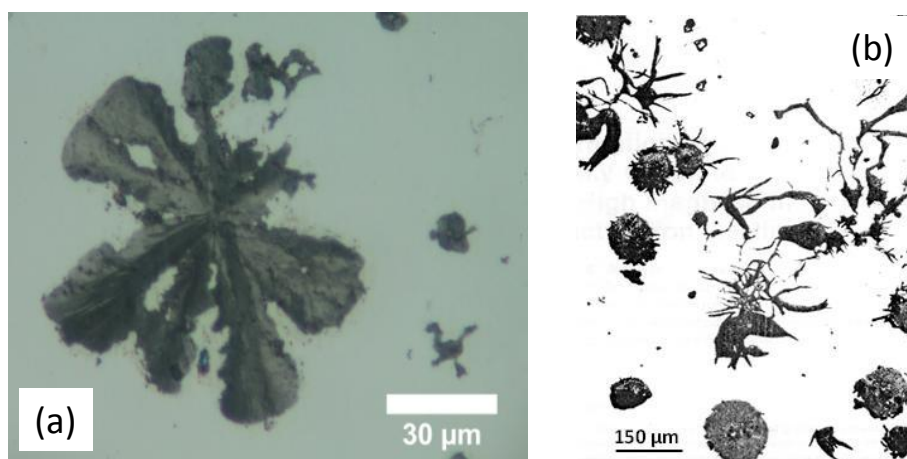


Figure 4. a: Exploded graphite spheroid (courtesy of R. Ghergu);
b: overgrowth of spiky graphite onto graphite spheroids [24].

The evidence for this interaction between dissolved magnesium in the liquid alloy and precipitating graphite was defended long ago by Merchant in a comprehensive review of the work on cast irons in the early 1960s [25]. However, it was challenged in the mid-1970s when Auger spectroscopy measurements failed to detect magnesium on graphite spheroids [26]. Advances in microanalysis have revealed the presence of magnesium in some cases but have also confirmed the absence of accumulation of this element at the graphite/matrix interface [27-29]. The lack of detection by Auger mentioned above would therefore be due to the detection limit of this technique (a few %) in the presence of a more diluted spatial distribution of magnesium than imagined.

To further understand the role of magnesium, it appeared interesting to study a spheroidal graphite cast iron doped with antimony. When added at a level of a few tens of ppm to spheroidal graphite cast iron, antimony leads to both a decrease of the diameter of the spheroids and a smoothing of their surface, and then to the development of protuberances. A SEM micrograph of a deep-etched sample showing a spheroid with protuberances is shown in figure 5a. Note the smoothing of the spheroid surface when compared to figure 3b. Further, antimony is known to strongly promote pearlite during the eutectoid transformation and this has been attributed to a Sb-rich layer at the graphite/matrix interface which has been evidenced by Auger analysis [30-32]. This pearlite-promoter effect has been understood to be due to the Sb-rich layer preventing the transfer of carbon to the graphite precipitates, which raises the question of when this layer forms.

As a matter of fact, antimony is known to be surface active in iron melts and, as such, is expected to segregate at the interface between graphite and matrix (either liquid or austenite) as it does at the surface of the melt if there is no more surface active element in the alloy. On the same sample as that illustrated in figure 5a, thin foils were prepared so as to analyse the graphite/matrix interface in an atomic resolution microscope. A 2-4 nm thick Sb-rich layer could be found at the interface of both the spheroids and the protuberances, as seen with the Sb map superimposed to the TEM micrograph in figure 5b. Some lead was also found but no trace of magnesium could be detected. It may be suggested that antimony accumulates progressively at the graphite/matrix interface during early solidification and repels magnesium from the interface, first limiting spheroidal growth and finally stopping it, thus forcing the development of protuberances for graphite to precipitate.

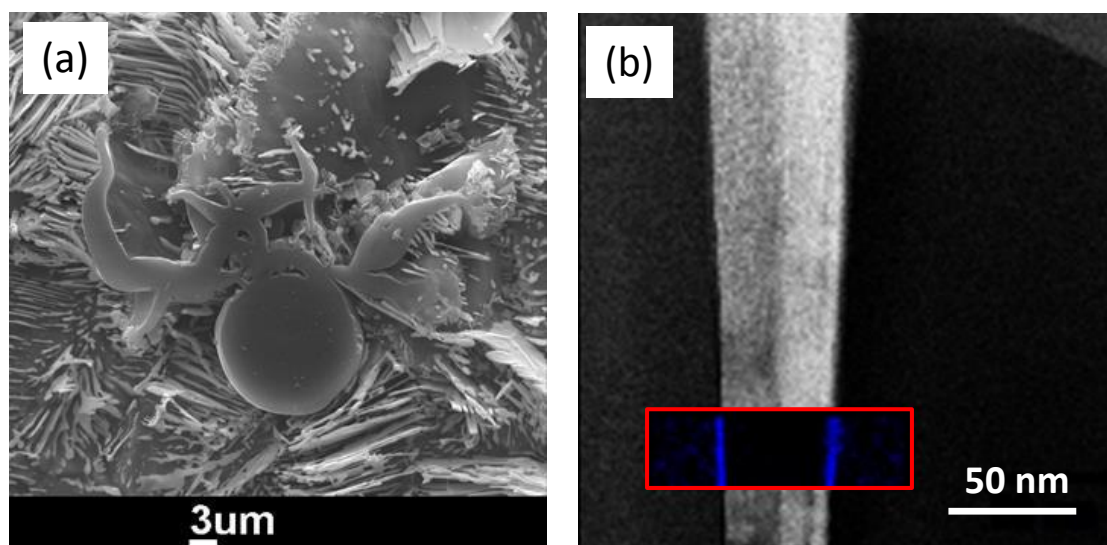


Figure 5. SEM micrograph of a Sb-doped spheroidal graphite cast iron showing spiky graphite growing out from a spheroid (a) and TEM bright field image of a protuberance with superimposed within the red rectangle the map of antimony.

Measurements of the surface tension and contact angle of cast iron drops on graphite have been recently re-analysed [33]. Adding magnesium to a melt decreases the amount of free sulphur and oxygen and thus increases its surface tension, but at the same time strongly decreases the work of adhesion. Turned the way round, melts leading to lamellar graphite are characterized by a high work of adhesion between melt and graphite that relates to the presence of sulphur. It could thus be concluded that the graphite shape is not only determined by the melt surface tension as sometimes stated, but that consideration of the work of adhesion is also needed. Further work is needed to understand how this works: adding Al to an S-bearing alloy increases surface tension while retaining high work of adhesion and the lamellar form, whereas adding antimony to a melt that has been

spheroidised decreases surface tension and retains low work of adhesion but leads to a spiky graphite that develops as lamellar graphite.

4. Conclusion

Analysis of the structure of graphite spheroids in cast iron suggested a growth scheme based on a mechanism of epitaxial 2D-nucleation of growth blocks at the surface of the spheroids that then grow parallel to the surface in the prismatic direction. Such a growth is hindered by adsorption of magnesium atoms without any build-up of this element. On the contrary, surface active elements such as sulphur and oxygen in non-spheroidized melts and antimony in magnesium-treated melts do segregate at the graphite/matrix interface, repelling magnesium and then leading to lamellar-type graphite growth.

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